On the average charge of the oxygen vacancy in perovskites necessary for kinetic calculations

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Abstract. An analytical result has been obtained for the value of the dynamical charge necessary for calculations of oxygen vacancy kinetics in dielectric perovskite-type crystals. It is shown by using the Berry phase analysis that this charge equals the nominal charge of the vacancy: for example, for the double charged state, it is 2; a neutral vacancy has the zero charge.

Oxygen vacancies in oxides of the perovskite family can be easily created or removed by thermal treatment in reduction or oxidizing atmosphere respectively [1]. The vacancies are always present in single crystals and even more so in ceramics and thin films. This nonstochiometry effects some properties of perovskite-type oxides: dielectric permittivity can have a noticeable [2, 3, 4] and sometimes even large [5] contribution from electrons connected with the oxygen vacancies; Second Harmonic Generation and luminescence experiments revealed a large effect of oxygen vacancies on the intensities [6, 7]; Electroconductivity of the samples is strongly dependent on the oxygen vacancy concentration an, hence, on thermal treatment [8].

Sometimes the presence of oxygen vacancies helps to improve properties of materials, for instance, it is possible to obtain extremely high dielectric permittivity in a wide temperature interval due to Maxwell-Wagner relaxation [5]. It happens that these unavoidable point defects spoil some properties, for example, in ferroelectric memory applications the presence of oxygen vacancies is thought to be crucial and results in the phenomenon called "fatigue" [9, 10]: ferroelectric thin films degrade after a large number of polarization switching due to the movement of the oxygen vacancies leading to the creation of large frozen internal fields preventing the switching process.

In order to study the last effect one can use kinetic equations describing a charge transport in a bias field [11]. Charged oxygen vacancies are thought to be moved in this field [9, 10]. For quantitative estimations one needs to know the oxygen vacancy charge Z and the field E_a acting on the vacancy. In review [12] this problem was discussed in details: there had been several trials to describe these quantities among which there are two very different proposals, one of them suggests using Lorentz's expression for the local field, $E_a = (\varepsilon + 2)E/3$, and the other assumes that each of the vacancies can be surrounded by a sphere and the field inside this sphere is described by an Onsager's expression: $E_a = 3\varepsilon/(2\varepsilon + 1)E$ where ε is dielectric permittivity and E being the bias macroscopic field. Scott and Dawber [12] criticized the first approach as giving an unrealistic diverging value of the local field at large ε inherent to ferroelectrics, and they suggested using the Onsager expression which much better suits experimental data.

In this letter I will show that the problem of choosing the local field and charge of the vacancy can be solved analytically with the help of a Berry phase analysis [13]. This approach rigorously considers not only the local field effect but also the covalent effect connected with the covalent binding of the ions. The resultant polarization is computed quantum mechanically by taking integrals over the Brillouin zone.

Instead of dealing with local fields it is easier to consider average, macroscopic, field. In this case the charge of the vacancy must be replaced by the dynamical charge

$$Z_{i\alpha,\beta}^* = \frac{\partial P_\alpha}{\partial r_{i\beta}} \tag{1}$$

where P_α is α-th component of polarization, and $r_{j\beta}$ is the displacement of i-th ion in the β-th direction. As the average field is uniform, only the dynamical charge should

be averaged over a path of the oxygen vacancy

$$Z = \frac{1}{l} \int Z^*_{V_O zz}(\mathbf{r}) dr \qquad (2)$$

where l is the length of this path; for the sake of simplicity, we directed the field along the z axis. By substituting definition (1) to the integral in (2) one has

$$Z = \frac{1}{l} \int \frac{\partial P_z}{\partial r_{V_O z}} dr = \frac{\Delta P_z}{l_z} \qquad (3)$$

where ΔP is the finite difference in polarization after performing the run over the path, and l_z is the z component of the displacement.

The difference in polarization ΔP is the sum of polarization stemming from the ionic charges transferred, $\Delta P_i = Z_i l_z$ where Z_i is the nominal (ionic) charge of the i-th particle, and the electronic polarization ΔP_e:

$$\Delta P_z = \Delta P_i + \Delta P_e \qquad (4)$$

The computation of the electronic (covalent) contribution can be carried out with the help of the Berry phase analysis [13]:

$$\Delta P_e \sim \Delta \varphi \qquad (5)$$

where φ is the average over the electronic bands Berry phase. The Berry phase strongly changes inside the unit crystal cell and it is a periodic function with respect to the displacement with the period coinciding with the lattice parameter.

Consider the path shown in Fig. 1. The initial and final states in this path have the same point symmetry and, consequently, the electronic contribution vanishes in this path: $\Delta P_e = 0$. In other words, at the displacements by a lattice constant or by a few lattice constants, the electronic contribution to the polarization vanishes and only the ionic contribution remains. This rigorously proves that the average dynamical charge of the oxygen vacancy equals its nominal charge; for example, for the double charged vacancy V_O'', this charge is 2, for the single charged vacancy it equals 1, and, finally, for the neutral vacancy it is zero.

It follows from the analyses performed that the Lorentz expression for the local field provides wrong result for the kinetics of oxygen vacancies in oxides. This expression gives a very large value which, in fact, reflects the fact of strong local field in the cenrosymmetric position of the simple cubic lattice made of polarizable ions. If one averages this field over the unit cell, as it was evenly suggested in Ref. [12] then the difference between the local field and the average one obviously vanishes at all. Notice that we have shown that it is enough even to average the result over any of the paths coinciding two points in the lattice with equal point symmetry. Hence the field averaged over such a path equals the field averaged over the unit cell volume. Close result can be obtained if one uses the Onsager expression at high ε: this result is only 3/2 times larger with respect to the right expression which uses the average field instead of the local one.

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Caption

Fig. 1. A path of the oxygen vacancy between equal points in the perovskite-type lattice. Large circles correspond to B ions in the ABO_3 perovskite structure, small ones to oxygens, and the square is the oxygen vacancy.